Local mode axis tilting in H_2S

M.S. Child[*], O.V. Naumenko[†], M.A. Smirnov[†] and L.R. Brown[‡]

[*]Physical and Theoretical Chemistry Laboratory,
South Parks Road, Oxford, OX1 3QZ, UK
[†]Institute of Atmospheric Optics, 513, Russian Academy of Sciences,
Tomsk, Russia
[‡]Jet Propulsion Laboratory, California Institute of Technology,
Pasadena, CA 91109, U.S.A.

Abstract

A physically intuitive non-resonant local mode axis tilting model for the interpretation of higher overtone bands of $X H_2$ species is outlined and illustrated by reference to the near-infrared of spectrum H_2S. Quantitative connections with the conventional normal mode resonance coupled picture are derived and local mode bawd expressions for the vibrational-rotational wavefunctions are given. Const ants are reported for the (31 1)-(212) and (302)-(203) bands at 11008NW1 and $12149\,cm^{-1}$ respectively.

I. Introduction

Despite the computational efficiency of conventional normal mode techniques for the analysis of rotational-vibrational spectra, the overtone bands of small symmetrical hydrides have certain features that favour an alternative local mode interpretation. In the first place local mode vibrational splittings can become small compared with rotational energy differences [1]. Secondly the conditions that allow vibrational localization also lead to local mode relationships between coefficients in the vibrational-rotational Hamiltonian [2]. Finally the change from normal mode to local mode character affects the vibrational interactions. Particular attention has been given to the effects of the H_{22} terms in the Hamiltonian because resonance coupling terms that are off diagonal in $q_1 q_3$ in normal coordinate terminology become vibrationally diagonal in an appropriate local mode representation [3-5], thereby contributing an inertial term that lowers the apparent symmetry of the species in question. The strength of Coriolis coupling is also found to be progressively quenched as the local mode limit is reached [6-8].

The first such local mode effects on rotational structure were reported for NH_3 by Ovchinnikova [3], and the clearest general formulation is by Lehmann [4]. The most striking results to date apply to XH_4 hydrides, which were predicted by normal mode simulations [2], to snow symmetric top rotational structure in their $|n000\rangle$ local mode bands. The observation of this effect, first for GeH_4 [9-10] and then for other species [11-14], was followed by a local mode interpretation [4,5] based on the use of bond coordinates combined with an inertial axis transformation to allow quantization around the uniquely excited bond. A detailed discussion of the spatial properties of the local mode based rotational eigenstates has also been given [15].

The present paper applies similar ideas to the overtone bands of XH_2 species, with particular reference to H_2S. Experimentally more than 30 bands are known for the ^{32}S isotope [16-23] and an accurate potential surface has been deduced [24]. Many of the higher bands show increasing evidence of the four-fold clustering associated with close local mode degeneracies in near symmetric tops [2,4,24]. The present paper was stimulated by the observation that, the onset of an increasingly strong $H_{22}(or$ $alpha)$ resonance between essentially degenerate pairs of local vibrational states leads to ambiguities in the rotational assignments. In addition, as discussed below, if the constraint to C_{2v} symmetry is relaxed, alternative assignments lead to an equally accurate non-resonant simulation and the resulting spectroscopic absorption bands have hybrid character. The physically intuitive explanation, which was first advanced by Lehmann is that elimination of the H_{22} resonance term can be accommodated by a tilting of tile inertial axes. The purpose of this paper is to develop the detailed theory of this local mode tilting effect.

The theory extends the work of Lukka and Halonen [25] but follows Lehmann [3] in transforming the quantization axis to lie perpendicular to the molecular plane, in order to facilitate the axis tilting argument. The angle of tilt is then shown to depend on the ratio between the H_{22} resonance term C_{xy} and the rotational constant asymmetry, $A_v -- B_v$, in the resonant-normal mode description. Expressions are given for the effective asymmetry in the uncoupled representation, local mode forms for the symmetrised rovibrational wavefunctions, the relative A type and B

2

type transit ion amplitudes and the first -order deviat ions from predict ed local mode vibrational-rotat ional degeneracies. Wang and Zhu [26] have recently considered t he effects of rot at ion on t hese near degeneracies by analysis of the wavefunct ion in the I^r represent at ion

The main results of t he paper are highlight ed in section 3. Finally the t heory is applied t o the overt one spect ra of H_2S in sect ion 4. The non-resonant local mode model is shown t o become superior t o t he convent ional Coriolis resonance model for the higher overtone bands, both for assignment purposes and for cwo1 1o1 h1 y in the number of fitting paramet ers. The relat ive advantages of t he AI^r and $AIII^r$ reduct ion schemes are also discussed. The former appears to be preferable fOr fitting purposes, but the latter gives rise to relatively unmixed wavefunct ions. The centrifugal distortion constants in the $AIII^r$ reduct ion are also found to be much less sensitive to the change from a resonant to a non-resonant model t han those in the AI^r reduct ion.

II. The local mode axis tilting model

The vibrational-rotational spectra of bent XH_2 species are normally analysed in the I^r axis system [27], with the molecule in the xz plane. It is however more convenient for present purposes to employ the III^r system, with z perpendicular to this plane (see Fig. 1), so that the axis tilt occurs around the quantization axis.

Some notes on non-standard aspects of t he not at ion may be helpful. The first and second quantum numbers in the loc al mode symbol $|nm\rangle$ refer to bonds r_a and r_b respectively, with the assumption that $n \gg m$. Symmetrised and antisymmet rised combinations are denoted as usual by $|nm\pm\rangle$. It is also useful to emphasise geomet-rical aspects of the axis tilting argument by recognising that r_a is the predominantly excited bond in state $|nm\rangle$ and r_b in t he state $|mn\rangle$ Thus the int roduct ion of alt er-native sumbols $|a\rangle$ and $|b\rangle$ for $|nm\rangle$ and $|mn\rangle$ respectively, allows the use for H_{aa} for the vibrationally averaged rotational Hamilt onian with inertial axes tilted in response to predominant excit at ion of r_a and similarly for H_{bb} and r_b. Corresponding notations $|J\,K\rangle_a$ and $|J\,K\rangle_b$ are adopted for symmetric top states defined with respect to the two tilted axis systems, while $|J\,K\rangle$ without a subscript, is used for states defined with respect, to the C_{2v} inertial axes.

The relevant leading t erms of t he vibrational-rot at ional Hamilt onian in t he III^r system take the form [25].

$$\hat{H}/hc = \hat{G}_v + A\hat{J}_x^2 + B\hat{J}_y^2 + C\hat{J}_z^2 \qquad (1)$$
$$- \bar{q}_1^2(\alpha_1^{(x)}\hat{J}_x^2 + \alpha_1^{(y)}\hat{J}_y^2 + \alpha_1^{(z)}\hat{J}_z^2) - \bar{q}_3^2(\alpha_3^{(x)}\hat{J}_x^2 + \alpha_3^{(y)}\hat{J}_y^2 + \alpha_3^{(z)}\hat{J}_z^2)$$
$$+ d_{13}q_1q_3(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x).$$

Complications due to interaction with the binding mode q_2 may well be impor-tant in practice, but they have no bearing on the tilting mechanism. The Coriolis term has also been omitted because it is known that $\zeta_{13}^{(z)} = 0$ (for our axis system) in the local mode limit [2,4,6]. Local mode axis tilting is at tribut ed to compet it ion between normal rotational asymmetry associat ed wit h the difference $(A - B)$ and the final H_{22} resonance term in equation (1), in circumstances where vibrational energy

3

differences arising from t he vibrational operator $\hat{G}_v$ are small compared with the term in d_{13}. The 2×2 matrix represent at ion of the vibrational operator $\hat{G}_v$ is diagonal in the normal mode represent at ion, with elements $\pm \epsilon$, and purely off-diagonal in t he local mode represent at ion, wit h elements ϵ.

Following previous authors [25] we replace t he scaled normal coordinat es (q_1, q_3) by bond displacements (r_a, r_b) so that, wit h $q_1 = (r_a + r_b) / \sqrt{2}, \ q_3 = (r_a - r_b) / \sqrt{2},$

$$\hat{H}/hc = \hat{G}_v + A\hat{J}_x^2 + B\hat{J}_y^2 + C\hat{J}_z^2 \tag{2}$$
$$- (\bar{r}_a^2 + \bar{r}_b^2)[\alpha_+^{(x)}\hat{J}_x^2 + \alpha_+^{(y)}\hat{J}_y^2 + \alpha_+^{(z)}\hat{J}_z^2]$$
$$- 2\bar{r}_a\bar{r}_b[\alpha_-^{(x)}\hat{J}_x^2 + \alpha_-^{(y)}\hat{J}_y^2 + \alpha_-^{(z)}\hat{J}_z^2]$$
$$+ \frac{1}{2} d_{13}(\bar{r}_a^2 - \bar{r}_b^2)(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x)$$

where

$$\alpha_{\pm}^{(\xi)} = \frac{1}{2}(\alpha_1^{(\xi)} \pm \alpha_3^{(\xi)}), \quad \xi = x, y, z \tag{3}$$

$$\bar{r}_i^2 = \frac{1}{2}(\beta r_i^2 + \hbar^2\beta^{-1}p_i^2) \qquad i = a, b \tag{4}$$

$$\bar{r}_a\bar{r}_b = \frac{1}{2}(\beta r_a r_b + \hbar^2\beta^{-1}p_a p_b) \tag{5}$$

The parameter β is the scaling parameter for harmonic oscillations of an individual bond:

$$\beta = 2(\pi c \omega_b / \hbar)^{\frac{1}{2}}, \tag{6}$$

where ω_b is the bond frequency.

The assumed vibrational near-degeneracy now permits tile introduction of bond localised states

$$|a\rangle = |nm\rangle, \qquad |b\rangle = |mn\rangle \tag{7}$$

in which the first and second quantum numbers specify excit ation in bonds r_a and r_b respectively, with $n \gg m$ in the local mode limit. The resulting vibrational matrix elements of $\hat{H}$ are conveniently expressed in t he forms

$$\hat{H}_{aa}/hc = A_v\hat{J}_x^2 + B_v\hat{J}_y^2 + C_v\hat{J}_z^2 + C_{xy}(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x) \tag{8a}$$

$$\hat{H}_{bb}/hc = A_v\hat{J}_x^2 + B_v\hat{J}_y^2 + C_v\hat{J}_z^2 - C_{xy}(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x) \tag{8b}$$

$$\hat{H}_{ab}/hc = \epsilon - 2\langle nm| \bar{r}_a\bar{r}_b |mn\rangle [\alpha_-^{(x)}\hat{J}_x^2 + \alpha_-^{(y)}\hat{J}_y^2 + \alpha_-^{(z)}\hat{J}_z^2] \tag{8c}$$

4

where

$$A_v = A - \langle r^2 \rangle \alpha_+^{(x)} \quad etc \tag{9}$$

$$C_{xy} = d_{13} \langle \delta r^2 \rangle \tag{10}$$

$$\langle r^2 \rangle_a = \langle nm | \bar{r}_a^2 + \bar{r}_b^2 | nm \rangle = \langle n | \bar{r}_a^2 | n \rangle + \mathbf{(m} | \bar{r}_b^2 | m \rangle \tag{11}$$

$$\langle \delta r^2 \rangle = \langle nm | \bar{r}_a^2 - \bar{r}_b^2 | nm \rangle = \langle n | \bar{r}_a^2 | n \rangle - \langle m | \bar{r}_b^2 | m \rangle \tag{12}$$

All other vibrational matrix elements are zero. Moreover the off-diagonal term H_{ab} also becomes vanishingly small in the local mode limit because both the local mode splitting, represented by 2ϵ in the present notation, and the α difference terms $\alpha_-^{(\xi)}, \xi = x, y, z$ tend to zero [2,4,6]. Secondly $\langle nm | \bar{r}_a \bar{r}_b | mn \rangle$ is subject to the selection rule $n - m = \pm 1$ in the harmonic limit and it is assumed that $n >> m$.

Equations *(8a), (8b), (10)* and *(12)* show that the H_{22} resonance term in normal mode theory appears in local mode theory as an off-diagonal inertial term, with a magnitude that depends on the disparity between the mean squared displacements of the two inequivalently excited bonds. The sign difference between *(8a)* and *(8b)* dictates an axis tilt to principal axes in one direction or the other according to whether r_a or r_b is the longer bond (see Fig. 1).

The transformation to the principal axes of H_{aa} may be expressed in the form

$$\begin{pmatrix} \hat{J}_x \\ \hat{J}_y \end{pmatrix} = \begin{pmatrix} \cos \eta & -\sin \eta \\ \sin \eta & \cos \eta \end{pmatrix} \begin{pmatrix} \hat{J}_x^{(a)} \\ \hat{J}_y^{(a)} \end{pmatrix} \tag{13}$$

$$\hat{J}_z = \hat{J}_z^{(a)}$$

where the superscript a designates principal axes in local mode state $|a\rangle$ $\hat{H}_{aa}$ itself reduces to

$$\hat{H}_{aa}/hc = \frac{1}{2} (A_v + B_v)(\hat{J}_x^{(a)2} + \hat{J}_y^{(b)2}) + C_v \hat{J}_z^{(a)2} \tag{14}$$

$$+ \frac{1}{2} (A - B)_{eff}(\hat{J}_x^{(a)2} - \hat{J}_y^{(a)2})$$

The quantities of η and $(A - B)_{eff}$ are given by

$$\tan(2\eta) = [4C_{xy}/(A_v - B_v)] \tag{15}$$

$$(A - B)_{eff} = [(A_v - B_v)^2 + 4C_{xy}^2]^{\frac{1}{2}} \tag{16}$$

Equations *(14)*- (17) were first given by Lehmann [4], but their consequences were not fully explored. The corresponding transformation of H_{bb} yields a form identical with equation *(15)*, apart from the obvious substitution of b for a throughout, and the sign of η, which specifies the orientation of the transformed axes is reversal. Fig. 1. which is derived from data in table 2 below, illustrates the two axis tilted states for the $|nm\pm, v_2 >= |40\pm, 1)$ states of H_2S. The effective A and B constants, given

5

by equation *(16)* are 1 $0.2007 cm^{-1}$ and $8.5689 cm^{-1}$ respectively and the tilting angle, given by equation *(15)* is $30.95°$.

The conclusion is that the H_{22} resonance term, which couples vibrational states of different symmetry in normal mode theory, can be transformed by local mode arguments to appear as an additional contribution to the specific rotational asymmetry $(A - B)_{eff}$. All rotational states are alsseen to be exactly doubly degenerate in the local mode limit; although the eigenfunctions of $\hat{H}_{aa}$ and $\hat{H}_{bb}$ will be shown below to differ by virtue of the difference in sign attached to the tilting angle η. This result also has a physically appealing interpretation in the sense that the 'normal' contribution $(A_v - B_v)$ to $(A - B)_{eff}$ may be associated with deviations of the bend angle from $90°$, because a rigid symmetric species with orthogonal bonds is an accidental symmetric top. Equations *(10)* and *(12)* show that the additional term C_{xy}^2 in equation *(16)* arises from a difference in mean squared displacements between the two bonds.

One must of course recognize that even the slightest deviation from strict local mode behavior will restore the proper symmetry or antisymmetry of the eigenstates. Hence it is convenient to express the eigenstates in the $J^{(a)}$ and $J^{(b)}$ representation to those in the original symmetrical J representation. To this end it may be noted from equation *(13)* that

$$\hat{J}_{\pm}^{(a)} = \hat{J}_x^{(a)} \pm i\,\hat{J}_y^{(a)} = e^{\pm i\eta} J_{\pm} \tag{17a}$$

while

$$\hat{J}_{\pm}^{(b)} = \hat{J}_x^{(b)} \pm i\,\hat{J}_y^{(b)} = e^{\mp i\eta} J_{\pm} \tag{17b}$$

Thus the phase modified basis functions

$$|J\,K\rangle_a = e^{i\eta K}|J\ K\rangle \tag{18a}$$

$$|J\,K\rangle_b = e^{i\eta K}|J\ K\rangle \tag{18b}$$

may be verified to satisfy the normal angular momentum relations.

$$J_z^{(i)}|J\ K\rangle_i = K|J\ K\rangle_i \tag{19}$$
$$J_{\pm}^{(i)}|J\ K\rangle_i = [J(J+1) - K(K \mp 1)]^{\frac{1}{2}}|J\ K-1\rangle_i$$

for $i = a, b$. Consequently the eigenfunctions of $\hat{H}_{aa}$ and $\hat{H}_{bb}$ may both be expressed in the form

$$|J\,K_a\,K_c\rangle_i = \sum_K C_{K\sigma}|J\ K\ \sigma\rangle_i \tag{20}$$

where the coefficients $c_{K\sigma}$ are independent of i and $|JK\sigma\rangle_i$ are the appropriate Wang combinations

$$|J\ K\ \sigma\rangle_a = (|J K\rangle_a + (-1)^\sigma |J-K\rangle_a)/(1 + \delta_{K0})^{\frac{1}{2}} \tag{21a}$$
$$= \cos(\eta K)|J\ K\ \sigma\rangle + i\sin(\eta K)|J\ K\ \sigma + 1\rangle$$

$$|J\ K\ \sigma\rangle_b = (|J K\rangle_b + (-1)^\sigma |J-K\rangle_b)/(1 + \delta_{K0})^{\frac{1}{2}} \tag{21b}$$
$$= \cos(\eta K)|J\ K\ \sigma\rangle - i\sin(\eta K)|J\ K\ \sigma + 1\rangle$$

The second line of equations (210) and (21b) have been derived with the help of equations (18a) and (18b,). K_c in equation (20) is equal to the K value of the leading term of the sum and K_a is even or odd according to the evenness or oddness of $(J + K_c + \sigma)$. Finally it remains to symmetrize the theory by combining equations (21a) and (21b) with appropriate vibrational fadors $|a\rangle = |nm\rangle$ and $|b\rangle = |mn\rangle$. The resulting symmetry adapted local vibrational-rotational eigenstates take the form

$$|J \ K_a \ K_c; \pm\rangle \ = \ \sum_K C_{K\sigma}[|JK\sigma\rangle_a \ |nm\rangle \pm |JK\sigma\rangle_b \ |mn\rangle]/\sqrt{2} \qquad (22)$$

$$= \ \sum_K C_{K\sigma}[\cos(\eta K)\,|J \ K \ \sigma\rangle\,|nm\pm\rangle$$

$$+ i \ \sin(\eta K)\,|J \ K \ \sigma + 1\rangle\,|nm\mp\rangle]$$

where $|nm\pm\rangle$ are the symmetry adapted vibrational states

$$|nm\pm\rangle = (|a\rangle \pm |b\rangle)/\sqrt{2} = (|nm\rangle \pm |mn\rangle)/\sqrt{2} \qquad (23)$$

Equation (22) is one of the main results of the theory.

Notice that the symmetrical form of equation (22) clearly separates the axis switching terms in ηK from the rotational basis fundions $|JK\sigma\rangle$ which ate quantized in the symmetrical (x, y, z) axis frame. Consequently the spectroscopic absorption intensities may be estimated in terms of normal Honl-London factors. Traditions from the ground vibrational state, denoted by $|0\rangle$, to the $|nm+\rangle$ and $|nm-\rangle$ states are polarised in the y and x direction respectively. Hence the dipole transition matrix elements may be expressed as

$$\langle 0|\,\mu\,|nm+\rangle \ = \ \mu_B\,\hat{y} \qquad (24)$$

$$\langle 0|\,\mu\,|nm-\rangle \ = \ \mu_A\,\hat{x}$$

where $\hat{x}$ and $\hat{y}$ are the angular parts of the transition amplitudes.
When combined with the form of the ground rotational eigenstate

$$|J''K_a''K_c''\rangle = \sum_{K''} C_{K''\sigma''}\,|J''K''\sigma''\rangle \qquad (25)$$

equations (22) - (2.5) imply that

$$\langle J''K_a''K_c''; 0|\,\mu\,|JK_aK_c; +\rangle \ = \ \sum_{K,K''} C_{K\sigma}C_{K''\sigma''}[\mu_B \ c\,\langle J''K''\sigma''|\,\hat{y}\,|JK\sigma\rangle \qquad (26a)$$

$$+ \mu_A \ s\,\langle J''K''\sigma''|\,\hat{x}\,|J \ K \ \sigma + 1\rangle]$$

while

$$\langle J''K_a''K_c''; 0|\,\mu\,|JK_aK_c; -\rangle \ = \ \sum_{K,K''} C_{K\sigma}C_{K''\sigma''}[\mu_A \ c\,\langle J''K''\sigma''|\ \hat{x}\,|JK\sigma\rangle \qquad (26b)$$

$$+ \mu_B \ s\,\langle J''K''\sigma''|\,\hat{y}\,|J \ K \ \sigma + 1\rangle],$$

7

where $c = cos(\eta K)$ and $s = sin(\eta K)$.

The form of equation *(22)* also allows a simple estimate of the first order effect of the vibrational oft-diagonal operator H_{ab}, which is assumed for simplicity to be dominated by the local mode splitting term ϵ in equation *(8c)*. The present assumption is that these off-diagonal terms are necessarily small compared with d_{13} tout they could never Mess be large compared with the asymmetry splitting of the high K_c rotational eigenvalues.

Bearing in mind that the vibrational operator $\hat{G}_\nu$ is diagonal in the symmetrised local mode states,

$$\langle nm+|\,\hat{G}_v\,|nm+\rangle = -\langle nm-|\,\mathbf{G}_{v}|nm-\rangle = \epsilon \tag{27}$$

and that $|JK\sigma\rangle$ and $|JK\sigma'\rangle$ in equation *(22)* are orthogonal, the first order corrections to the energies oft he previously degenerate rotational-vibrational states $|JK_aK_c;\pm\rangle$ are thereby deduced to be

$$\langle JK_aK_c;\pm|\,\hat{G}_v\,|JK_aK_c;\pm\rangle = \pm\epsilon\sum_{K}C_{K\sigma}^2(\cos^2(\eta K)-\sin^2(\eta K)) \tag{28}$$

$$= \pm\epsilon\sum_{K}C_{K\sigma}^2\cos(2\eta K)$$

In other words the axis tilting, which is measured by the angle η, serves to quench the local mode splitting from its purely vibrational value. The possibility of such local mode enhancement by rotation was first suggested by Lehmann[4]. Wang and Zhu [26] reach similar conclusions for H_2S in the I^r representation by performing less physically transparent rotations about the y axis.

III. Implications of the model

The above axis tilting model is not primarily offered as a new computational tool, because for example the effects of centrifugal terms have been omitted. The intention is rather to provide a new framework for t he interpretation of computational and experiment al results.

The first consideration in t he local mode limit is that the rotational analysis of excited q_1 and q_3 states be carried forward *equivalently* either with or wit bout a constraint to impose C_{2v} symmetry. The resulting parameters in the former case will be 'normal' rotational constants A_v, B_v and C_v and a Coriolis resonance parameter C_{xy} (or C_{xz} in I^r rot at ion). The second approach on the other hand will yield only t hree rotational parameters $\frac{1}{2}(A_v+B_v)$, C_v and an asymmet ry term $(A - B)_{eff}$, given according to equation *(16)* t)y

$$(A - B)_{eff} = [(A_v - B_v)^2 + 4C_{xy}^2]^{\frac{1}{2}} \tag{29}$$

Strict double degeneracy in all rotational-vibrational energy levels is also predict ed in the local mode limit.

A second implication of the theory is that t he loss of information inherent in a three parameter simple vibrational stat e anlaysis as distinct from a four paramet cr

coupled vibrational one. can in principle be remedied by a careful intensity analysis, because equations *(26a)* and *(26b)* show that t he transition amplitudes are modified by t erms dependent on the axis tilt ing angle η. which depends according to (15) on the ratio of C_{xy} to $(A_v - B_v)$.

The final conclusion is that t he introduction of a vibrational energy split t ing between t he t wo 10GII mode states, which is small compared with the anharmonic resonance paramet er C_{xy}, will serve to lift t he rot ational-vibrational degeneracy of all other stat es in accordance with t he formula in *(29)*. It would be int cresting to find cases in which η could be deduced by use of equation *(29)*.

One should also notice that a fully coupled version of the t heory could be obtained by including t he vibrationally off-diagonal operator $\hat{H}_{ab}$ given by equation *(8c)*. The necessary matrix elements would however i n v o l v e phase factors $e^{\pm 2i\eta K}$ arising from overlap bet ween $|JK\rangle_a$ and $|JK\rangle_b$, as given by *(18a)* and *(18b)*. The hermitian character of the resulting Hamiltonian matrix is therefore computationally less convenient than the conventional real normal mode form.

IV. Local mode axis tilting in H₂S

Tile local mode character of the overtone bands of H_2S is well attest ed on the basis of the 30 different analysed bands [14-21]. In particular the local mode splittings for the $|nm\pm; v_2\rangle = |30\pm;$ O) and $|30\pm;$ 1) stat es at $7576cm^{-1}$ and $8697cm^{-1}$ are reported [22] as O.163C~/I- ^{1} and $0.013cm^{-1}$ respectively, while these for the corresponding $|40\pm; v_2 >$ stat es at $9911cm^{-1}$ and 11009cm- ^{1} arc less than 0.001 cm^{-1}. The α_- values derived from a global fit of the analysed bands ($\alpha_-^{(a)} = -0.016$, $\alpha_-^{(b)} = 0.016$ and $\alpha_-^{(c)} =$ O 008cm^{-1}) are also small enough t o justify neglect of the off-diagonal operator H_{ab} in equation *(8c)*, compared with $C_{xy} \simeq 0.5 - 0.6cm^{-1}$. Experimental details of the bands which are discussed below are listed in table 2.

As a direct test of the theory in section 2, the previously reported $|40\pm;$ O) and $|40\pm;1\rangle$ bands (corresponding to (301)-(202) and (311)-(212) in conventional notation) [22] were reanalysed in the III^r representation, both as resonantly coupled interacting pairs and as isolated hybrid bands. The derived spectroscopic parameters arc given in table 2. It is evident that the quality of the fit is, if anyt hing, slightly better for the isolat ed state analysis, despite the reduction from 10 to 9 parameters. The isolated state A and B rotational constants are also seen to be well approximated by the estimated values it 1 parent hoses, which were derived from t he A_v, B_v and C_{xy} constants by means of equation (16). Finally the remaining parameters differ by only a few percent in going from one form of analysis to the other.

It is also interesting to perform a similar comparison between 'int tract ing stat e' and 'isolat ed state' analyses in the I^r represent at ion, which is normally preferred for H_2X species. Relevant data for the $|40\pm;1\rangle$ and $|50\pm;$ O) (or (31 1)-(212) and (203)-(302)) energy levels with $J \leq 8$ are given in t able 3; more ext ensive data for these local mode pairs will be published elsewhere [28]. Notice that the assignments are much more straightforward in the isolated band picture because the energy increases monotonically with increasing K_a, whereas there are numerous examples of inverted level posit ions when t he stat es are t reated as int eracting pairs. The resulting spec-

troscopic parameters in table 4 again show t hat t he isolated band analyses achieve a better fit to the (311)-(212) bands with one fewer parameter, and an equally good fit for tile (302)-(203) bands with nine fewer parameters (assuming that four levels that are perturbed by dark states ['23] and poorly determined levels with $J \leq 11$ were excluded from the fit). Estimated A_{eff} and B_{eff} constants, obtained by substituting C_{xz} for C_{xy} in equation (16) are in excellent agreement with the optimised values for the isolated state fit to the (311)-(212) band, and also with the corresponding entries given for the III^r analysis in table 2. The agreement is less good for the (302)-(203) band, possibly due to the assumed influence of pert urbations during the fit [23]. The final observation is that the 'interacting state' analyses lead to drastically different values for the distortion constants, when the analysis is performed in the I^r representation, whereas only minor changes occurred in the III^r representation.

In comparing the two represent ations, it is seen, as expected, that the rms deviations for (311)-(212) band is smaller in the I^r than in the III^r representation. On the other hand the rational for the isolated band, axis tilting, analysis is much clearer from the III^r viewpoint. Secondly the relative insenitivity of the distortion constants to changes between the 'interacting state' and 'isolated state' pictures in the III^r representation, suggests that these constants have greater physical significance than those obtained by the I^r fitting procedure.

V. Conclusions

Previously known local mode transformations to the conventional normal mode rotation-vibrational Hamiltonian [25] have been extended, by transformation to the III^r representation, to show that t he conventional Coriolis coupled rotational analysis between two degenerate vibrational states (in the local mode limit,) is equivalent to two degenerat c isolated state analyses applicable t o molecules with C_s symmetry, with inertial axes tilt ed either clockwise or anticlockwise with respect t o the equilibrium symmetry axes. Equations (15) and (16) give expressions for the angle of tilt, η, and the effective A and B crest ants for the isolated state analysis, in terms of the conventional A_v, B_v rotational and C_{xy} resonance constants. The angle of tilt is also related to the difference between mean squared vibrational amplit udes of the two bonds. Local mode t ype expression for t he vibrational-rot at ional wavefunctions are given in equat ion (22) and used t o derive formulae for the A type and B t ype t ransition amplitudes oft he hybrid bands in t erms oft he angle oft ilt and conventional Honl-London factors. A further result, given in equat ion (29), is that t he vibrational-rotational level split t ings are predict ed t o be quenched from their purely vibrational values in a manner dependent on t he product ηK_c.

Applications of the theory to t he (301)-(202) and (302)-(203) t)ands of H_2S fully support the above pict ure. New 'isolated band' analyses for the (31 1)-(212) and (302)-(203) bands were also performed in the traditional I^r represent at ion. The fit to observed data is superior to that obt ained by the usual H_{22} coupled model, and t he number of derived parameters is reduced. In comparing t he I' and III^r representa- t ions, it found that t he former gives a bet ter fit t o t he data, but that the distort ion parameters obtained by t he I^r analysis differ (Drastically according to whether the

'coupled state' or 'isolated state' models were used. By contrast only minor changes to the distortion cent ants arise in the III^r representation. The conclusion is that the I^r representation is superior for fit t ing purposes, but that parameters derived from the III^r representation may have greater physical significance.

VI. Acknowledgements

VII. References

[1]   M.S. Child and I,. Halonen, (1984), Adv.Chem.Phys. 57,1.

[2]   L. Halonen and A.G. Robiett c, (1986), J.Chem.Phys., 84, 6861.

[3]   M. Ya. Ovchinnikova, (1988), Chem.Phys.Lett., 120, 249

[4]   K.K.Lehmann, (1991), J.Chem.Phys., 95, 2361.

[5]   M.S. Child and Q. Zhu, (1991), Chem.Phys.Lett., 184, 41.

[6]   L. Halonen, (1987), J.Chem.Phys., 86, 588.

[7]   L. Halonen, (1987), J.Chem.Phys., 86, 31 15.

[8]   M.S. Child and Q. Zhu, (1983), Chem.Phys.Lett., 207, 116.

[9]   Q. Zhu, B.A. Thrush and A.B. Robiette, (1988), Chem.Phys.Lett. **150**, 181.

[10]   Q. Zhu, B.A. Thrush, (1990), J.Chem.Phys., 92, 2691.

[11]   M. Halonen, 1,. Halonen, H. Bürger and S. Sommer, (1990), J.Chem.Phys., 93, 1607.

[12]   M. Halonen, L. Halonen and H. Bürger, (1993), Chem.Phys.Lett ., **205**, 380.

[13]   M. Halonen, L. Halonen, H. Bürger and P. Moritz, (1991), J.Chem.Phys., 95, 7099.

[14]   M. Halonen, I,. Halonen, H. Bürger and P. Moritz, (1993), Chem.Phys.Lett., 203, 157.

[15]   K.K.Lehmann, (1992), J.Chem.Phys., 96. 7402.

[16]   1,.1,. Strew> (1983), J.Mol.Spectrosc., 97,9.

[17]   W.C. Lane, 'l'. II. Edwards, J. I{. Gillis, F.S. Bonomo and F.J. Murcray, (1985), J.Mol.Spectrosc. , 111, 320.

[18]   L. Lechuga-Fossat, J-M. Flaud, C. Camy-Peyret and J.W.C. Johns, (1994), Can.J. Phys.,**62**, 1889.

[19]   L.E. Snyder and 'l'. II. Edwards, (1969), J.Mol.Spectrosc., 31, 347.

[20]   O.V. Zotov, V.S. Makarov, O.V. Naumenko and A.D. Bykov, (1991),

Atmos.Opt., 4, 798.

[21]   L. Lechuga-Fossat, J - M . Flaud, C. Camy-Peyret, P. Arcas and M. Cuisenier, (1987), Mol.Phys., 61, 23.

[22]   A.D. Bykov, O.V. Naumenko, M. A. Smirnov, L.N. Sinitsa, L.R. Brown, J. Crisp and D. Crisp, (1994), Can.J. Phys., 72, 989.

[23]   J-M. Flaud, R. Grosklos, S.B. Rai, R. St uber, W. Demt roder, D.A. Z'ate, L-G. Wang and Th.F. Gallagher, (1995), J.Mol.Spectrosc. 172, 275.

[24]   I.N. Kozin and P. Jensen, (1994), J.Molec.Spectros. 163, 483.

[25]   'T. Lukka and L. Halonen, (1 994), J.Chem.Phys., 101, 8380.

[26]   X. Wang and Q. Zhu, (1996), J.Chem.Phys., 105, 8011.

[27]   J.K.G. Watson in 'Vibrational Spectra and Structure', (1977), (J.R. Durig, Ed.,) Vol.6, pp. 1-80, Elsevier, Amsterdam.

[28]   O.V. Naumenko, L.R. Brown. L.N. Sinitsa and M.A. Smirnov (in preparation).

12

Figure caption

Fig. 1. Schematic representation of the degenerate isolated titled axis states. The tilting angle $\eta \sim 31$" is consistent with the constants A_x, B_x and C_{xy} for the (3 11) - (212) states of H_2S in table 2. The large symbol for one of the atoms indicates the more excited bond.

Table 1

Vibrational States of H_2S Studied

Local mode notation $nm \pm v_2$	Resonating Pairs C_{2v} Symmetry	Band Centres cm^{-1}	Ref.	Precision of energies cm^{-1}	Instrument and Resolution
40± 0	(301), (202)	9911.	20	0.003	FTS 0.021 cm^{-1}
40± 1	(311), (212)	11008.	20	**0.003**	FTS 0.021 cm-'
50± 0	(302), (203)	12149.	I 21		diode laser 0.01 cm^{-1}

Table 2

Spectroscopic parameters (cm^{-1}) of the $|40\pm;0>$ and $|40\pm;1>$ or [(30 I) - (202) and (3 I I) - (2 12)] vibrational states of the H$_2$S molecule from the resonance and nonresonance fitting using a Watson-type III^r Hamiltonian

	(301)-(202)	Isolated	Estimated	(3 I 1)-(212)	Isolated	Estimated
E$_v$	991 1.02470(280)	991 1.02600(260)		11008.69100(230)	11OO8.69IOO(2IO)	
A	9.689976(420)	9.871477(390)	(9.879)	9.980428(42)	10.200505(440)	(10.184)
B	8.539932(420)	8.357874(350)	(8.351)	8.789340(420)	8.5692 11(340)	(8.584)
c	4.4742 15(100)	4.4752867(900)		4.4143399(950)	4.4143973(780	
D$_k$10^3	0.78381(150)	0.75940(1 10)		1.09390(280)	1.0723(140)	
D$_{,k}$10^2	-0.16956(160)	-0.16628(100)		-0.216790(270)	-0.2 1528(140)	
D$_J$10^3	0.974893(750)	0.96655(1 10)		1. 147299(700)	1. 144248(700)	
d$_k$ 103	0.16170(660)	o. I 594(400)		O. I386(105)	0.1229(490)	
d, 103	0.1 1541(380)	0.09088(290)		0.19802(480)	0.14049(390)	
C$_{xy}$	0.4914878(150)			0.557708(130)		
J$_{max}$	13	13		13	13	
N levels	141	70		139	70	
N param.	10	9		10	9	
RMS deviation	0.00956	0.00899		0.00697	0.00690	

Table 3

Two methods for the assignment of the experimental rotational energy levels (cm⁻¹) $\cdot$ the $|40\pm;1\rangle$ and $|50\pm;0\rangle$ or $[(311), (212), (203)$ and $(302)]$ vibrational states of the H₂S molecule.

$J\ K_a\ K_c$	C_{2v} symmetry (w)(2 2) Eobs	C_s symmetry (isolated) Eobs	dE	C_{2v} symmetry (203)(302) Eobs	C_s symmetry (isolated) Eobs	dE
0 0 0	11008.684	11008.6843	-3	12149.4603	12149.458	-0
1 0 1	11021.669	11021.6697	0	12161.9961	12161.9937	-1
1 1 1	11027.451	11027.4573	2	12167.4002	12167.4009	-1
2 0 2	11045.107	11044.7*6	-2	12185.0*59	12184.5773	-4
2 1 2	11044.711	11045.1116	1	12184.5736	12185.0342	-3
2 1 1	11057.555	11057.5557	0	12196.18*0	12196.878	6
2 2 1	11062.44	11062.4430	-5	12201.2424	12201.2452	0
2 2 0	11065.355	11065.3574	2	12203.7256	12203.7200	-5
3 0 3	11076.336	11076.27	-1	12215.7963	12215.7130	0
3 1 3	11076.272	11076.3359	1	12215.7929	12215.7929	1
3 1 2	11099.518	11099.5178	0	12236.8084	12236.7344	6
3 2 2	11101.356	11101.3519	-1	12236.7424	12238.8037	-8
3 2 1	11111.604	11111.6043	-2	12247.754	12247.7583	11
3 3 1	11121.299	11121.2ww	-2	12257.76*8	12257.7691	-1
3 3 0	11122.980	11122.9800	-1	12259.1012	12259.1024	-4
4 0 4	11116.506	11116.5065	3	12255.4946	12255.4880	-3
4 1 4	11116.506	11116.5105	0	12255.4880	12255.4946	-8
4 1 3	11150.641	11150.2400	4	12286.7393	12286.7390	13
4 2 3	11150.237	11150.2w2	1	12286.2227	12286.2264	0
4 2 2	76.5	71.6721	1	12310.757	12305.3847	12
4 3 2	11171.672	76.5123	-4	12305.37 6	12310.7599	-2
4 3 1	11184.166	84 67	-0	12317. 369	12317.1*54	-1
4 4 1	11199.955	99.9555	-1	12333.4 7	12333.4079	2
4 4 0	11200.783	1200.77*4	-0	2ww40 06	12334.0 50	6
5 0 5	11200.783	65.52	2	2ww40 06	12304.0392	0
5 0 5	65.524	65.52	1	12344.0479	12343.9452	4
5 1 5	11165.524	11165.524				
5 1 4	11209.286	209.21 9	0	12344.0426	12344.0426	4
5 2 4	11209.210	11209.2880	7	12343.9454	12344.0426	4
5 2 3	11243.297	1 243.293	1	12375.2349	12375.2390	-5
5 2 4	11241.756	1241.75 .6	-10	237*w≶72w	12373.3790**	
5 w w	11241.756	11241.753	3	237*w≶72w	12375.2390	-5
5 w 2	27o 732	11261 *04	-7	12401.0633	12390.6598	-8
5 4 2	1126 .18	.27o.7w .3	0	12390.6535	12401.0666	-8
5 4 1	11275.775	11275.7697	-2	12*5-o*79	12404.9975	-12
5 5	11298.449	11298.4480	1	12428.2442	12428.2398	2

Table 3 (continued)

```
5 5 0 11298.811 11298.809 11298.8089 2 12428.4895 12428.4859 12428.4859 6
6 0 6 11223.333 1 1223.333 11223.3354 -1 12361.3717           "12361.3659 -6
6 1 6 11223.333 1 1223.333 11223.3354 -1          12361.3659 12361.3717 -1
6 1 5 11276.817 11276.819 11276.8184 7            12410.2618 12410.2585 14
6 2 5 11276.819 1 1276.817 11276.8184 -1          12410.2585 12410.2618 2
6 24  11320.100                          12449.8293 12449.8175 12449.3636-11
6 3 4 ]1319,744 1 1319.744 11320.0998**    12449.3651 12449.3636 12449.8175-11
6 3 3 11354.269 11354.262 11350.2448 -4 12481.3684 12481.3780 12476.5408-15
64 3 11350.243 11350.247 11354.2711 9              12476.5408 12481.3780 0
64 2 11384.114              11368.4030 5 12509.9425 12509.9423 12493.0830 13
6 5 2 11368.402 11368.403 11384.1134 -7 12493.0816 12493.0830 12509.9423 -1
6 51 11387.009             11387.0198 3 12512.0324 12512.0307 12512.0307 2
6 6 1             11416.738 11416.7372 2 12542.3038 12542.3041 12542.3041 -4
6 60 11416.881             11416.8797 -O 12542.3952 12542.4009 12542.4009 2
7 07 11289.949 11289.949 11289.9534 2              12427.4965 12427.4843 -5
7 1 7 11289.949 11289.949 11289.9534 2 12427.4843          12427.4965 6
71 6 11353.152 11353.152 11353.1529 -3             12485.2758 12485.2787 8
7 2 6 11353.152 11353.152 11353.1529 -5 12485.2787          12485.2758 3
7 2 5             11405.9555 0              12533.6118 12533.5294 0
7 3 5 11405.953                          12533.5193 12533.5294 12533.6118 -2
7 3 4             1I447.6106**              12572.7779 12571.2726 4
7 4 4 11447.610                            12571.2726 12572.7779 10
7 43              11475.3738 5             12605.3499 12605.3499**
7 5 2                                      12637.5655 12637.5655**
7 6 2             11516.7720 -2
7 6 1             11518.2451 3             12638.6048 12638.6048**
7 7 1 11554.720   11554.7187 -5 12675.6536 12675.6453 12675.6453 -1
7 7 0             11554.786 11554.7847 5   12675.6787 12675.6787 0
8 0 8 11365.350 11365.350 11365.3511 0
8 1 8 11365.350 11365.350 11365.3511 0             12502.3755 12502.3755 -3
8 1 7 11438.263 11438.263 11438.2675 -1 12569.0563          12569.0434 -2
8 2 7 11438.263 11438.263 11438.2675 -1            12569.0434 12569.0563 10
8 2 6                          12626.2254 12626.2199 12626.2199 -l
8 3 6 11500.728                            12626.2201 12626.2201-15
8 3 5                                      12673.9107 12673.5502-10
8 4 5                                      12673.5502 12673.9107 6
```
----

*) Rotational energy levels for C2V assignment were taken
   from Ref. 20 for(311) and (2 12) sates and from Ref.21
   for (203) and (302) states.

dE=(Eobs-Ecalc)x 1000 cm- 1for Cs symmetry energy levels

**- Levels were excluded from the fitting.

Table 4

Spectroscopic parameters (cm^{-1}) of the $|40\pm;1>$ and $|50\pm;0>$ or [(3 1)-(212) and (203)-(302)] vibrational states of the H$_2$S molecule from resonance and nonresonance fitting using a Watson-type I^r Hamiltonian

	(311)-(212) ref.[20]	Isolated	Estimated	(302)-(203) ref. [21]	Isolated	Estimated
E	11008.6836	11008.68747(130)		12149.4580	12149.45744(280)	
A$_v$	9.92916	10.202834(380)	(10,20125	9.4749975	9.819851(790)	(9.71755)
B,	8.84191	8.570033(1 10)	(8.56981)	8.471912	8.128625(300)	(8.22935)
C$^{\prime\prime}$	4.41553	4.4138781(330)		4.4111438	4.409495(130)	
D$_k$10'	0.4067	0.12893(230)		0.4443236	0.03337(450)	
D$_{jk}$10^4	-23.682	-0.8027(420)		-26.12636	6.735(160)	
D$_j$10^3	0.65609	0.449906(280)		0.575537	0.27681(120)	
d$_k$10'	-0.06	0.78487(250)		-0.439822	0.6281(100)	
d, 10'	0.29705	0.193521(150)		0.2547141	0. 104021(760)	
H$_k$10^5	0.283	0.3381(300)		0.46069	0.7920(610)	
h$_k$10^5				0.1229	-0.3643(490)	
C$_{xz}$	0.608171			0.549675		
J$_{max}$	9	14		14	11	
N levels	129 (for both states)	84		128 (for both states)	77	
N param.	9	10		20	11	
RMS deviation	**0.005**	**0.0038**		**0.0074**	**0.0074**	